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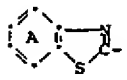
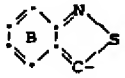
(54) Disperse and acid azo dyes having 1,2-dihydroquinoline couplers

(57) New dyes of formula (I) give blue to green shades on polyamide fibres:

D–N = N–C′ (I)

wherein C′ is an optionally substituted 1,2-dihydroquinoline coupler, and D is selected from:



and


wherein rings A and B are optionally substituted.

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Formulae in the printed specification were reproduced from drawings submitted after the date of filing, in accordance with Rule 20(14) of the Patents Rules 1982.

SPECIFICATION

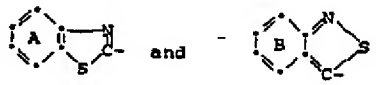
Disperse and acid azo dyes having 1,2-dihydroquinoline couplers

This invention concerns disperse and acid dyes particularly suited for the dyeing of polyamide fibres, and having the general formula

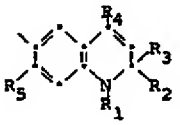
$$D - D = N - C^1$$

wherein D is 2-benzothiazolyl or 3-benzisothiazolyl, unsubstituted or substituted with 1–3 substituents such as acyl, acylamido, alkyl, carboalkoxy, alkyl-SO_3M acylamido, halogen, and cyano and C^1 is a 1,2-dihydroquinoline coupler which is unsubstituted or substituted.

More particularly the dyes correspond to the formula above wherein D is selected from



wherein rings A and B may have 1–3 substituents independently selected from alkyl, cyclohexyl, aryl, alkoxy, thiocyano, alkylthio, arylthio, cyano, nitro, $CONH_2$, CONHalkyl, $CON(alkyl)_2$, alkoxycarbonyl, alkanoyl, aroyl, alkanoyloxy, alkylsulfonyl, SO_2NH_2, $SO_2NHalkyl$, $SO_2N(alkyl)_2$, alkyl-SO_3M, alkylsulfonamido, acylamido, halogen, trifluoromethyl, SO_3-aryl, SO_3-alkyl, and alkenyl of 2–8 carbons; and C^1 is represented by the formula



R_1 is H, alkyl, aryl or cyclohexyl;

R_2 and R_3 are each independently selected from H and alkyl;

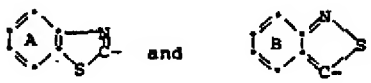
R_4 is H, alkyl, or alkyl-SO_3M; and

R_5 is selected from H, alkyl, alkoxy, alkenyl of 2–8 carbons, halogen, acylamido, alkylthio and formamido, wherein the alkyl moieties thereof may be substituted with 1–3 substituents independently selected from hydroxy, halogen, cyano, alkoxy, alkylthio, alkanoyl, alkanoyloxy, and alkoxycarbonyl;

wherein all of the alkyl, alkylene, alkenyl and cyclic moities in the defined substituents for rings A and B, and for R_1 may themselves be substituted with 1–3 substituents different from the said moiety and independently selected from hydroxy, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl (C_4H_3O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO_2NH_2, $SO_2NHaryl$, SO_2N-Halkyl, $SO_2N(alkyl)_2$, alkyl-SO_3M, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido ($C_4H_4O_2N$), glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), 1-(2-pyrrolidono) (C_4H_6ON), cyano, $CONH_2$, CONHalkyl, $CON(alkyl)_2$, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl and arylsulfonyl; and wherein each M is selected from H, Na, K, NH_4, $\frac{Ca}{2}$, $\frac{Zn}{2}$

and the colorless cations of salts of primary, secondary and tertiary aliphatic and aryl amines.

Preferred of the present dyes are where D is selected from



wherein rings A and B are unsubstituted or substituted with 1–3 substituents independently selected from cyano, alkylsulfonyl, SO_2NH_2, $-NO_2$, alkyl-SO_3M, $SO_2NHalkyl$, $SO_2N(alkyl)_2$, and halogen.

The various alkyl or alkylene moieties in, for example, alkoxy, alkanoyl, and alkoxyalkoxy, within the above definitions of R_1-R_5 and the A and B ring substituents, have 1–6 carbons, and they and the alkenyl groups are straight or branched chain.

The dyes of this invention impart blue to green shades on fibers, particularly polyamides, exhibiting improvements in one or more properties such as fastness to light, ozone, perspiration, oxides of nitrogen, washing, sublimation or crocking, and in leveling, transfer, pH stability, exhaustion, build and non-red flaring, and the acid dyes are surprisingly bathochromic.

The diazo components useful in this invention are prepared according to procedures well known to the art. The present dyes may be applied to polyamide fibers by conventional dyeing procedures, e.g., dispersed in a lignin sulfonate and dyed at 98°C. on nylon fabric for one hour from an aqueous bath. The following examples illustrate procedures which are generally applicable for preparation of the present couplers and dyes.

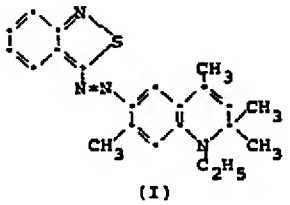
EXAMPLE 1

(a)—*Procedure For the Preparation of 1,2-Dihydro-2,2,4,7-Tetramethylquinoline*

Meta-toluidine (535 g.) and iodine (6 g.) are charged to a 2 liter, 3 neck, round bottom flask. The reaction is heated to 155°C. and about 3,500 g. of acetone is added at 155–160°C. beneath the surface over a 12 hour period. A mixture of acetone and water distills off during the addition. The reaction mixture is heated one-half hour at 160°C. and then distilled to about 690 g. of 1,2-dihydro-2,2,4,7-tetramethylquinoline boiling at 107–111°C. at 0.55 mm., a 74% yield. This product is then ethylated with triethylphosphate in the presence of ethyl iodide in known manner.

(b)—*Diazotization and Coupling*

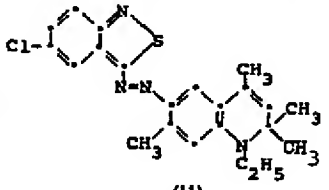
Sodium nitrite (0.72 g., 0.0104 mole) was added to sulphuric acid (5.0 cc.) and the solution warmed to 70°C., for 5 minutes. 1–5 Acid, a propionic-acetic acid mixture (1:5 molar ratio) (10.0 cc.) was added below 20°C. The mixture was cooled to 0°C. and 3-amino-2,1-benzisothiazole (1.50 g., 0.01 mole) was added, followed by a further 10.0 cc. of 1–5 acid. The mixture was stirred at 0–5°C. for two hours and then added to the coupler of Example 1 (10.75 g., 0.05 mole) in 50% aqueous ethanol (54.0 cc.) containing sodium acetate (2.05 g.), at <5°C. After stirring at 0–5°C. for one hour the dye was warmed to room temperature and precipitated by adding to cold water. The product was filtered and washed well with water to yield 2.61 g. (69.5%) of the final dye product, I.



(I)

EXAMPLE 2

By application of the above Example 1(b) procedure, Dye II was prepared in 63% yield.



(II)

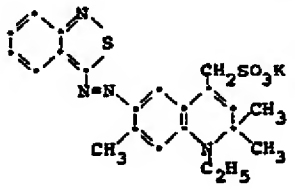
The preparation of the sulfonated 1,2-dihydroquinoline is given in German Offen. 3,005,874 (C.A. *94*, 15593K, 1981) and comprises sulfonating the 4-alkyl-1,2-dihydroquinoline with H_2SO_4, $ClSO_3H$, and/or SO_3 and converting, if desired, the acid group to its salt in known manner.

The acid dyes of the invention may be applied to polyamide fiber by the following method: The test dye, as a mixture with a sulphate such as ammonium sulfate, is pasted with boiling water and then made up to a known volume with water to give a weight ratio of water to dye of 30:1. Four percent on weight of fiber (owf) of a lignin sulphonate leveling agent is added, followed by ammonium acetate (about 3.0% owf) to adjust the pH to 6. The initial dyeing temperature is 40°C. which is raised to the final dyeing temperature of 98°C. over 30 minutes. The dye bath is held at 98°C. for 60 minutes, then cooled, and the test fabric given a warm water rinse and air drying.

EXAMPLE 3

Sodium nitrite (0.72 g., 0.0104 mole) was added to sulphuric acid (5.00 cc.) and the solution warmed to 70°C., for 5 minutes. Ten cc. of 1–5 acid was added, at less than 20°C.

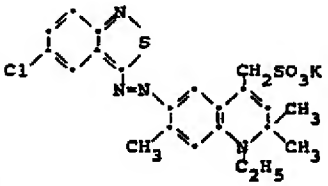
The mixture was cooled to 0°C. and 3-amino,2,1-benzisothiazole (1.50 g., 0.01 mole) was added, followed by a further 10.00 cc. of 1:5 acid. The mixture was stirred at 0–5°C. for two hours then added to the potassium salt of 1-ethyl-2,2,7-tri-methyl-1,2-dihydroquinolin-4-yl-methyl sulfonic acid (3.33 g., 0.01 mole) in 11 cc. of water at <5°C. This yielded 3.36 g. (68.0%) of the final dye product (III).



(III)

EXAMPLE 4

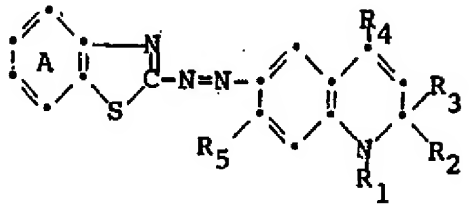
By application of the above procedure, in Example 4, Dye (IV) was prepared in 3.44 g. (65.0%) yield.



(IV)

The following tables further show specific dyes of the present invention which are prepared as above.

TABLE 1



Substituents on Ring A	R_5	R_2	R_3	R_4	R_1
None	H	H	H	H	H
None	H	H	CH_3	CH_3	C_2H_5
5,6-di-CH_2CH_2OH	CH_3	CH_3	CH_3	CH_3	C_3H_7-n
6-$CH_2OC_6H_5$	CH_2CH_2OH	CH_3	CH_3	CH_3	C_4H_9-n
6-$CH_2CH_2OC_6H_{11}$	CH_2Cl	H	$CH(CH_3)_2$	CH_3	$CH_2CH_2SO_2NHC_6H_5$
5-NO_2	OCH_2Cl	H	CH_3	CH_3	$CH_2CH_2OC_6H_5$
6-CH_2COOCH_3	OCH_3	H	CH_3	CH_2SO_3K	CH_3
5-$CH_2(C_4H_3O)$	OCH_3	H	CH_3	$CH_2CH_2SO_3Na$	C_6H_5
6-$CH_2CH_2OOCC_6H_5$	CH_2CH_2CN	H	CH_3	H	C_6H_{11}
6-CH_2OOCCH_3	CH_2SO_3Na	H	CH_3	CH_3	$C_2H_4OC_6H_{11}$
6-$SCH_2SO_2NH_2$	Cl	H	CH_3	CH_3	$CH_2CH_2SO_2NH_2$

6-CH_3	H	H	CH_3	$CH_2SO_3N\ H(Et)_3$	CH_2CH_2OH
6-$CONHCH_3$	OCH_3	C_2H_5	C_2H_5	C_2H_5	$CH_2CH_2SO_2N(C_2H_5)_2$
6-$CON(C_2H_5)_2$	NHCHO	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
6-$CH_2SO_2NHCH_3$	$NHCOCH_2OCCH_3$	CH_3	CH_3	CH_3	CH_2CN
6-C_6H_5	$NHCOCH_2CH_3$	C_3H_7-n	C_3H_7-n	H	CH_2CONH_2
6-CH_3	$NHCOCH_2Cl$	CH_3	CH_3	H	$CH_2CONHCH_3$
5-$CH_2NHCOOCH_3$	$NHCOC_6H_5$	CH_3	CH_3	H	$CH_2CON(C_2H_5)_2$
6-SCN	$NHCOC_2H_5$	C_4H_9-n	C_4H_9-n	H	$CH_2NHCOCH_3$
6-$CH_2NHCONHCH_3$	$NHCOC_6H_{11}$	CH_3	CH_3	H	$CH_2NHCOOCH_3$
6-OCH_3	H	CH_3	CH_3	H	CH_2OOCCH_3
6-Br	CH_2SCH_3	H	CH_3	H	$CH(C_4H_6ON)$
6-CF_3	$CH_2CH{=}CH_2$	H	H	H	$CH_2CH_2COOCH_3$
6-OCH_2CH_3	Br	H	CH_3	$CH_2SO_3(Ca/2)$	$CH_2CH_2COOCH_3$
6-SCH_3	I	H	CH_3	$CH_2SO_3(Zn/2)$	H
6-SCN	F	H	CH_3	$CH_2SO_3NH_4$	$C_2H_4SC_2H_5$
6-SO_2NH_2	SCH_3	H	CH_3	CH_3	C_3H_7-n
6-$SO_2NHC_4H_9$-n	CH_2OOCCH_3	H	CH_3	CH_3	C_4H_9-n

6-$SO_2N(CH_3)_2$	OCH_3	H	CH_3	CH_3	$C_2H_4C_6H_5$
6-$SO_3C_6H_5$	CH_3	H	CH_3	$CH_2N\ H(CH_2CH_2OH)_3$	$C_2H_4C_6H_{11}$
6-CN	H	H	H	H	CH_2Cl
6-$CONH_2$	$CH_2CH_2COOCH_3$	H	CH_3	CH_3	C_6H_4-p-OCH_3
4-$COOCH_3$	$CH_2CH(OH)CH_2OH$	H	CH_3	CH_3	C_6H_{10}-p-OH
6-$COCH_3$	CF_3	H	CH_3	CH_3	C_2H_5
6-COC_6H_5	CF_3	H	CH_3	CH_3	$CH_2CH_2SC_6H_5$
6-Cl	H	C_2H_5	C_2H_5	CH_3	$CH_2CH_2SO_2CH_3$
5,6-di-Cl	H	C_2H_5	C_2H_5	CH_2SO_3K	$CH_2CH_2SO_2C_6H_5$
4-Br	$CH_2CH(Cl)CH_2Cl$	C_2H_5	C_2H_5	CH_2SO_3H	$CH_2CH_2OC_2H_4OC_2H_5$
4-CF_3	$CH_2CH(OCH_3)CH_2OCH_3$	CH_3	CH_3	CH_3	$CH_2(C_8H_4O_2N)$
6-$NHCOCH_3$	CH_3	CH_3	CH_3	CH_3	CH_2CONH_2
6-SO_2CH_3	CH_3	CH_3	CH_3	CH_3	$CH_2(C_4H_4O_2N)$
6-$CH_2SO_2NHC_2H_5$	CH_3	CH_3	CH_3	CH_3	$CH_2CON(C_2H_5)_2$
6-$CH_2SO_2N(C_2H_5)_2$	CH_3	CH_3	CH_3	CH_3	$CH_2NHCONHCH_3$
6-$SO_2NHC_2H_5$	H	CH_3	CH_3	CH_3	$CH_2NHSO_2CH_3$
6-$CH_2CH_2NHCOCH_2Cl$	H	CH_3	CH_3	CH_3	CH_2OOCCH_3

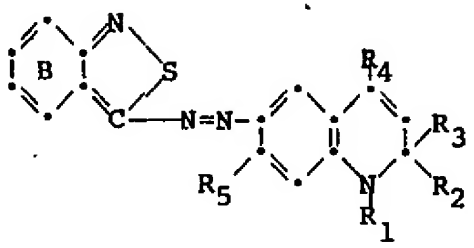
6-$CH_2NHSO_2CH_3$	CH_3	CH_3	CH_3	CH_3	$CH_2(C_4H_3O)$
6-$CH_2CH_2CH_2(C_4H_6ON)$	CH_2CH_2OH	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
None	CH_2Cl	CH_3	CH_3	H	$CH_2CH_2OOCC_6H_5$
6-CH_2CH_2CN	OCH_2Cl	CH_3	CH_3	C_3H_7-n	H
6-$NHCOCH_2CN$	OCH_3	CH_3	CH_3	C_3H_7-n	C_2H_5
6-$CH_2(C_4H_4O_2N)$	OCH_3	CH_3	CH_3	C_2H_5	C_3H_7-n
6-$CH_2(C_5H_6O_2N)$	CH_2CH_2CN	CH_3	CH_3	C_2H_5	C_4H_9-n
6-$CH_2CH_2(C_8H_4O_2N)$	Cl	CH_3	CH_3	C_2H_5	C_2H_5
5-CH_2CONH_2	Cl	CH_3	CH_3	CH_3	C_2H_5
6-$CH_2CONHCH_3$	H	CH_3	CH_3	CH_3	CH_3
6-$CH_2CH_2OCH_2CH_2OC_2H_5$	OCH_3	CH_3	CH_3	CH_3	C_6H_5
6-$COOCH_2CH_2OCH_3$	NHCHO	CH_3	CH_3	CH_3	C_6H_{11}
6-$CH_2CH_2SCH_3$	$NHCOCH_2OCCH_3$	CH_3	CH_3	CH_3	C_2H_5
6-$CH_2CH_2CH_2Cl$	$NHCOCH_2CH_3$	H	H	H	CH_2CH_2OH
6-$CH_2SC_6H_5$	$NHCOCH_2Cl$	H	CH_3	CH_3	CH_2CH_2OH
5-$CH_2SO_2CH_3$	$NHCOC_6H_5$	CH_3	CH_3	CH_3	CH_2CH_2OH
6-$CH_2SO_2C_6H_5$	$NHCOC_2H_5$	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$

6-$CH_2CH(OH)CH_2OH$	$NHCOC_6H_{11}$	H	$CH(CH_3)_2$	CH_3	CH_2CN
6-$CH_2CH(OH)CH=CH_2$	H	H	CH_3	CH_3	CH_2CONH_2
4-C_6H_4-p-OH	CH_2SCH_3	H	CH_3	H	$CH_2CONHCH_3$
5-C_6H_4-p-C_2H_5	$CH_2CH=CH_2$	H	CH_3	H	$CH_2CON(C_2H_5)_2$
6-C_6H_4-p-OC_6H_5	Br	H	CH_3	H	$CH_2NHCOCH_3$
6-C_6H_4-p-C_6H_{11}	I	H	CH_3	CH_3	$CH_2NHCOOCH_3$
6-C_6H_4-p-(C_4H_3O)	F	H	CH_3	CH_3	CH_2OOCCH_3
6-C_6H_4-p-OCC_6H_5	SCH_3	H	CH_3	CH_3	$CH_2(C_4H_6ON)$
6-C_6H_4-o-$COOCH_3$	CH_2OOCCH_3	C_2H_5	C_2H_5	C_2H_5	$CH_2CH_2COCH_3$
6-C_6H_4-m-SO_2NH_2	OCH_3	CH_3	CH_3	CH_3	$CH_2CH_2COOCH_3$
6-C_6H_4-p-$CONH_2$	CH_3	CH_3	CH_3	CH_3	H
6-C_6H_4-p-$NHCONHCH_3$	H	C_3H_7-n	C_3H_7-n	H	C_2H_5
5-C_6H_4-m-($C_8H_4O_2N$)	$CH_2CH_2COOCH_3$	CH_3	CH_3	H	C_3H_7-n
5-C_6H_3-o,p-di-CN	$CH_2CH(OH)CH_2OH$	CH_3	CH_3	H	C_4H_9-n
6-C_6H_2-o,m,p-tri-Cl	CF_3	C_4H_9-n	C_4H_9-n	H	C_2H_5
6-C_6H_4-p-$OCH_2CH_2OCH_3$	CF_3	CH_3	CH_3	H	C_2H_5
6-C_6H_4-p-SC_6H_5	H	CH_3	CH_3	H	CH_3

5-C_6H_4-p-SO_2CH_3	H	H	CH_3	H	C_6H_5
5-C_6H_4-p-$SO_2C_6H_5$	$CH_2CH(Cl)CH_2Cl$	H	H	H	C_6H_{11}
5-C_6H_{10}-p-Cl	$CH_2CH(OCH_3)CH_2OCH_3$	H	CH_3	CH_3	C_2H_5
6-C_6H_9-o,p-di-OH	CH_3	H	CH_3	CH_3	CH_2CH_2OH
6-C_6H_{10}-p-CH_3	CH_3	H	CH_3	CH_3	CH_2CH_2OH
6-C_6H_{10}-p-OC_2H_5	CH_3	H	CH_3	CH_3	CH_2CH_2OH
6-$CH_2CH_2SO_2NHC_6H_5$	CH_3	H	CH_3	CH_3	$CH_2CH_2OC_2H_5$
6-C_6H_4-p-$SO_2NHC_6H_5$	H	H	CH_3	CH_3	CH_2CN
6-$CH_2CH_2OCH_2C_6H_5$	H	H	CH_3	CH_3	CH_2CONH_2
5-C_6H_{11}	H	H	CH_3	CH_3	C_6H_4-p-($C_4H_4O_2N$)
5-SC_6H_5	H	H	CH_3	CH_3	C_6H_{10}-p-OCH_3
6-$OOCCH_3$	CH_3	CH_3	CH_3	CH_3	C_6H_4-p-Cl
6-SO_3-CH_3	CH_3	CH_3	CH_3	CH_3	$CH_2(C_5H_6O_2N)$
6-SO_3K	CH_3	CH_3	CH_3	CH_3	C_2H_5
6-SO_3N H$(Et)_3$	CH_3	CH_3	CH_3	CH_3	CH_2CH_2OH

$5-NO_2$	CH_3	CH_3	CH_3	C_2H_5
6-Cl	CH_3	CH_3	CH_3	C_2H_5
$5-NO_2$	CH_3	CH_3	$CH_2NH(C_2H_5)_3$	C_2H_5
6-Cl	CH_3	CH_3	CH_2SO_3K	C_2H_5

TABLE 2



Substituents on Ring B	R_5	R_2	R_3	R_4	R_1
None	H	H	H	H	H
None	H	H	CH_3	CH_3	C_2H_5
5,6-di-CH_2CH_2OH	CH_3	CH_3	CH_3	CH_3	C_3H_7-n
5-$CH_2OC_6H_5$	CH_2CH_2OH	CH_3	CH_3	CH_3	C_4H_9-n
6-$CH_2CH_2OC_6H_{11}$	CH_2Cl	H	$CH(CH_3)_2$	CH_3	C_2H_5
6-NO_2	OCH_2Cl	H	CH_3	CH_3	C_2H_5
6-CH_2COOCH_3	OCH_3	H	CH_3	CH_2SO_3K	C_6H_3-o,p-di-Cl
5-$CH_2(C_4H_3O)$	OCH_3	H	CH_3	$CH_2CH_2SO_3Na$	C_6H_4-p-$CONH_2$
5-$CH_2CH_2OOCC_6H_5$	CH_2CH_2CN	H	CH_3	H	C_6H_{10}-p-OH
5-CH_2OOCCH_3	CH_2SO_3Na	H	CH_3	CH_3	C_6H_4-m-OCH_3
5-$SCH_2SO_2NH_2$	Cl	H	CH_3	$CH_2SO_3N\ H(Et)_3$	CH_2CH_2OH

5-CH_3	H	H	CH_3	CH_3	C_6H_4-p-SCH_3
5-$CONHCH_3$	OCH_3	C_2H_5	C_2H_5	C_2H_5	C_6H_4-p-SO_2CH_3
5-$CON(C_2H_5)_2$	NHCHO	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
5-$CH_2SO_2NHCH_3$	$NHCOCH_2OCCH_3$	CH_3	CH_3	CH_3	C_6H_4-p-SO_2NHCH_3
5-C_6H_5	$NHCOCH_2CH_3$	C_3H_7-n	C_3H_7-n	H	CH_2CONH_2
6-CH_3	$NHCOCH_2Cl$	CH_3	CH_3	H	C_6H_4-m-$SO_2N(C_2H_5)_2$
5-$CH_2NHCOOCH_3$	$NHCOC_6H_5$	CH_3	CH_3	H	$CH_2CON(C_2H_5)_2$
6-SCN	$NHCOC_2H_5$	C_4H_9-n	C_4H_9-n	H	$CH_2NHCOCH_3$
6-$CH_2NHCONHCH_3$	$NHCOC_6H_{11}$	CH_3	CH_3	$CH_2SO_3(Ca/2)$	$CH_2NHCOOCH_3$
6-OCH_3	H	CH_3	CH_3	$CH_2SO_3(Zn/2)$	CH_2OOCCH_3
5-Br	CH_2SCH_3	H	CH_3	$CH_2SO_3NH_4$	$CH(C_4H_6ON)$
5-CF_3	$CH_2CH=CH_2$	H	H	H	$CH_2CH_2COOCH_3$
5-OCH_2CH_3	Br	H	CH_3	CH_3	$CH_2CH_2COOCH_3$
5-SCH_3	I	H	CH_3	CH_3	H
5-SCN	F	H	CH_3	CH_3	C_2H_5
5-SO_2NH_2	SCH_3	H	CH_3	$CH_2N\ H(CH_2CH_2OH)_3$	C_3H_7-n
5-$SO_2NHC_4H_9$-n	CH_2OOCCH_3	H	CH_3	CH_3	C_4H_9-n

5-$SO_2N(CH_3)_2$	OCH_3	H	CH_3	CH_3	C_2H_5
5-$SO_3C_6H_5$	CH_3	H	CH_3	CH_3	C_2H_5
5-CN	H	H	H	H	CH_3
5-$CONH_2$	$CH_2CH_2COOCH_3$	H	CH_3	CH_3	C_6H_5
4-$COOCH_3$	$CH_2CH(OH)CH_2OH$	H	CH_3	CH_3	C_6H_{11}
6-$COCH_3$	CF_3	H	CH_3	CH_3	C_2H_5
6-COC_6H_5	CF_3	H	CH_3	CH_2SO_3K	CH_2CH_2OH
6-Cl	H	C_2H_5	C_2H_5	CH_2SO_3H	CH_2CH_2OH
5,6-di-Cl	H	C_2H_5	C_2H_5	CH_3	CH_2CH_2OH
4-Br	$CH_2CH(Cl)CH_2Cl$	C_2H_5	C_2H_5	CH_3	$CH_2CH_2OC_2H_5$
4-CF_3	$CH_2CH(OCH_3)CH_2OCH_3$	CH_3	CH_3	CH_3	CH_2CN
5-$NHCOCH_3$	CH_3	CH_3	CH_3	CH_3	CH_2CONH_2
5-SO_2CH_3	CH_3	CH_3	CH_3	CH_3	$CH_2CONHCH_3$
5-$CH_2SO_2NHC_2H_5$	CH_3	CH_3	CH_3	CH_3	$CH_2CON(C_2H_5)_2$
5-$CH_2SO_2N(C_2H_5)_2$	CH_3	CH_3	CH_3	CH_3	$CH_2NHCOCH_3$
5-$SO_2NHC_2H_5$	H	CH_3	CH_3	CH_3	$CH_2NHCOOCH_3$
5-$CH_2CH_2NHCOCH_2Cl$	H	CH_3	CH_3	CH_3	CH_2OOCCH_3

5-$CH_2NHSO_2CH_3$	CH_3	CH_3	CH_3	CH_3	$CH_2(C_4H_6ON)$
5-$CH_2CH_2CH_2(C_4H_6ON)$	CH_2CH_2OH	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
None	CH_2Cl	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
5-CH_2CH_2CN	OCH_2Cl	CH_3	CH_3	C_3H_7-n	H
5-$NHCOCH_2CN$	OCH_3	CH_3	CH_3	C_3H_7-n	C_2H_5
5-$CH_2(C_4H_4O_2N)$	OCH_3	CH_3	CH_3	C_2H_5	C_3H_7-n
5-$CH_2(C_5H_6O_2N)$	CH_2CH_2CN	CH_3	CH_3	C_2H_5	C_4H_9-n
5-$CH_2CH_2(C_8H_4O_2N)$	Cl	CH_3	CH_3	C_2H_5	C_2H_5
5-CH_2CONH_2	Cl	CH_3	CH_3	CH_3	C_2H_5
6-$CH_2CONHCH_3$	H	CH_3	CH_3	CH_3	CH_3
6-$CH_2CH_2OCH_2CH_2OC_2H_5$	OCH_3	CH_3	CH_3	CH_3	C_6H_5
5-$COOCH_2CH_2OCH_3$	NHCHO	CH_3	CH_3	CH_3	C_6H_{11}
5-$CH_2CH_2SCH_3$	$NHCOCH_2OCCH_3$	CH_3	CH_3	CH_3	C_2H_5
5-$CH_2CH_2CH_2Cl$	$NHCOCH_2CH_3$	H	H	H	CH_2CH_2OH
5-$CH_2SC_6H_5$	$NHCOCH_2Cl$	H	CH_3	CH_3	CH_2CH_2OH
5-$CH_2SO_2CH_3$	$NHCOC_6H_5$	CH_3	CH_3	CH_3	CH_2CH_2OH
5-$CH_2SO_2C_6H_5$	$NHCOC_2H_5$	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$

5-$CH_2CH(OH)CH_2OH$	$NHCOC_6H_{11}$	H	$CH(CH_3)_2$	CH_3	CH_2CN
6-$CH_2CH(OH)CH=CH_2$	H	H	CH_3	CH_3	CH_2CONH_2
4-C_6H_4-p-OH	CH_2SCH_3	H	CH_3	H	$CH_2CONHCH_3$
5-C_6H_4-p-C_2H_5	$CH_2CH=CH_2$	H	CH_3	H	$CH_2CON(C_2H_5)_2$
5-C_6H_4-p-OC_6H_5	Br	H	CH_3	H	$CH_2NHCOCH_3$
5-C_6H_4-p-C_6H_{11}	I	H	CH_3	CH_3	$CH_2NHCOOCH_3$
5-C_6H_4-p-(C_4H_3O)	F	H	CH_3	CH_3	CH_2OOCCH_3
5-C_6H_4-p-OCC_6H_5	SCH_3	H	CH_3	CH_3	$CH_2(C_4H_6ON)$
5-C_6H_4-o-$COOCH_3$	CH_2OOCCH_3	C_2H_5	C_2H_5	C_2H_5	$CH_2CH_2COCH_3$
5-C_6H_4-m-SO_2NH_2	OCH_3	CH_3	CH_3	CH_3	$CH_2CH_2COOCH_3$
5-C_6H_4-p-$CONH_2$	CH_3	CH_3	CH_3	CH_3	H
5-C_6H_4-p-$NHCONHCH_3$	H	C_3H_7-n	C_3H_7-n	H	C_2H_5
5-C_6H_4-m-($C_8H_4O_2N$)	$CH_2CH_2COOCH_3$	CH_3	CH_3	H	C_3H_7-n
5-C_6H_3-o,p-di-CN	$CH_2CH(OH)CH_2OH$	CH_3	CH_3	H	C_4H_9-n
6-C_6H_2-o,m,p-tri-Cl	CF_3	C_4H_9-n	C_4H_9-n	H	C_2H_5
5-C_6H_4-p-$OCH_2CH_2OCH_3$	CF_3	CH_3	CH_3	H	C_2H_5
6-C_6H_4-p-SC_6H_5	H	CH_3	CH_3	H	CH_3

5-C_6H_4-p-SO_2CH_3	H	H	CH_3	H	C_6H_5
5-C_6H_4-p-$SO_2C_6H_5$	$CH_2CH(Cl)CH_2Cl$	H	H	H	C_6H_{11}
5-C_6H_{10}-p-Cl	$CH_2CH(OCH_3)CH_2OCH_3$	H	CH_3	CH_3	C_2H_5
5-C_6H_9-o,p-di-OH	CH_3	H	CH_3	CH_3	CH_2CH_2OH
5-C_6H_{10}-p-CH_3	CH_3	H	CH_3	CH_3	CH_2CH_2OH
5-C_6H_{10}-p-OC_2H_5	CH_3	H	CH_3	CH_3	CH_2CH_2OH
5-$CH_2CH_2SO_2NHC_6H_5$	CH_3	H	CH_3	CH_3	$CH_2CH_2OC_2H_5$
5-C_6H_4-p-$SO_2NHC_6H_5$	H	H	CH_3	CH_3	CH_2CN
5-$CH_2CH_2OCH_2C_6H_5$	H	H	CH_3	CH_3	CH_2CONH_2
5-SO_3K	H	H	CH_3	CH_3	C_2H_5
5-SO_3N H(Et)$_3$	H	H	CH_3	CH_3	CH_2CH_2OH
5,6-di-Cl	CH_3	CH_3	CH_3	CH_3	C_2H_5
5,6-di-Cl	CH_3	CH_3	CH_3	CH_2SO_3Na	C_2H_5

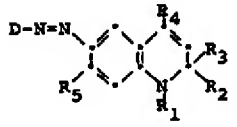
CLAIMS

1. A dye of the formula

$$D - N = N - C^1$$

wherein D is unsubstituted or substituted 2-benzothiazolyl or 3-benzisothiazolyl and C^1 is an unsubstituted or substituted 1,2-dihydroquinoline coupler.

2. A dye according to claim 1 wherein the coupler C^1 is of the formula



wherein R_1 is H or a group selected from alkyl, aryl and cyclohexyl, which groups are unsubstituted or substituted with 1–3 substituents different from the said group and independently selected from hydroxy, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl, aroyloxy, alkoxycarbonyl, alkanoyloxy, SO_2NH_2, alkyl-SO_3M, $SO_2NHaryl$, $SO_2NHalkyl$, SO_2N-$(alkyl)_2$, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido, glutarimido, phthalimido, 1-(2-pyrrolidono), cyano, $CONH_2$, CONHalkyl, $CON(alkyl)_2$, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl and arylsulfonyl;

R_2 and R_3 are each independently selected from H and alkyl;

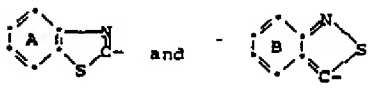
R_4 is H, alkyl, or alkyl-SO_3M; and

R_5 is selected from H, alkyl, alkoxy, alkenyl of 2–8 carbons, halogen, acylamido, alkyl-thio and formamido, wherein the alkyl moieties thereof are unsubstituted or substituted with 1–3 substituents independently selected from hydroxy, halogen, cyano, alkoxy, alkylthio, alkyl-SO_3M, alkanoyl, alkanoyloxy, and alkoxycarbonyl, wherein M is selected from H, Na, K, NH_4,

$$\frac{Ca}{2}, \frac{Zn}{2}$$

and the colorless cations of salts of primary, secondary and tertiary aliphatic and aryl amines.

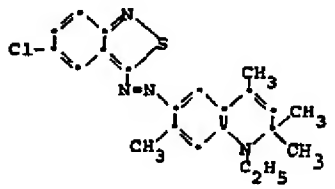
3. A dye of Claim 1 or 2 wherein D is selected from



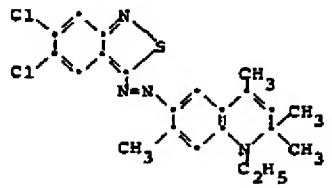
wherein rings A and B are unsubstituted or substituted with 1–3 substituents independently selected from alkyl, cyclohexyl, aryl, alkoxy, thiocyano, alkylthio, arylthio, cyano, $CONH_2$, CONHalkyl, $CON(alkyl)_2$, alkoxycarbonyl, $-NO_2$, alkanoyl, aroyl, alkanoyloxy, alkylsulfonyl, SO_2NH_2, $SO_2NHalkyl$, $SO_2N(alkyl)_2$, alkyl-SO_3M, alkylsulfonamido, acylamido, halogen, trifluoromethyl, SO_3-aryl, SO_3-alkyl, and alkenyl of 2–8 carbons, and wherein all of the alkyl, cyclohexyl and aryl moieties of the above groups are unsubstituted or substituted as for R_1.

4. A dye according to claim 3 wherein rings A and B are unsubstituted for substituted with 1–3 substituents independently selected from cyano, alkylsulfonyl, SO_2NH_2, $-NO_2$, $SO_2NHalkyl$, alkyl-SO_3M, $SO_2N(alkyl)_2$, and halogen.

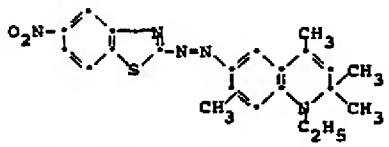
5. A dye of Claim 1 of the formula



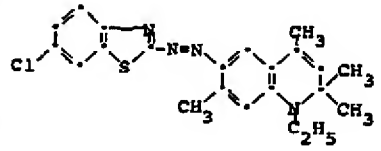
6. A dye of Claim 1 of the formula



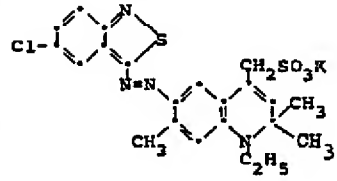
7. A dye of Claim 1 of the formula



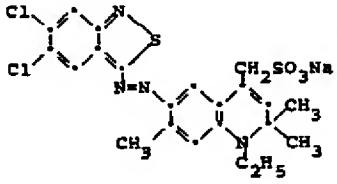
8. A dye of Claim 1 of the formula



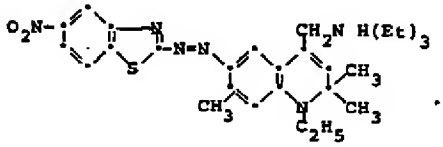
9. A dye of Claim 1 of the formula



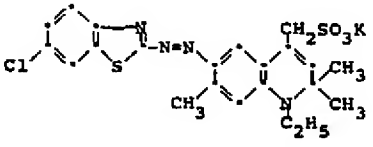
10. A dye of Claim 1 of the formula



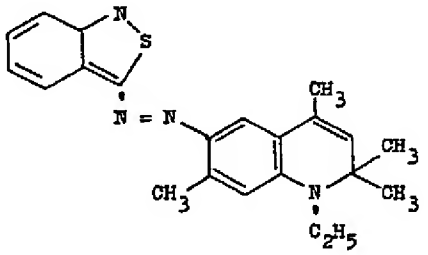
11. A dye of Claim 1 of the formula



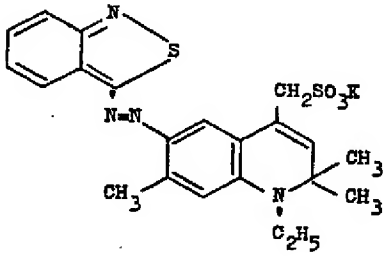
12. A dye of Claim 1 of the formula



13. A dye of Claim 1 of the formula



14. A dye of Claim 1 of the formula



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